

# Variational methods, multiprecision and nonrelativistic energies

V.I. Korobov

*Joint Institute for Nuclear Research,  
141980, Dubna, Russia*

It is known that the variational methods are the most powerful tool for studying the Coulomb three-body bound state problem. However, they often suffer from loss of stability when the number of basis functions increases. This problem can be cured by applying the multiprecision package designed by D.H. Bailey. We consider the variational basis functions of the type  $\exp(-\alpha_n r_1 - \beta_n r_2 - \gamma_n r_{12})$  with complex exponents. The method yields the best available energies for the ground states of the helium atom and the positive hydrogen ion as well as many other known atomic and molecular systems.

1. The development of the variational method for the Coulomb bound state problem can be traced using as an example the ground state of the helium atom. In early days when computers were big and very expensive the search proceeded mainly in the direction of making expansion of the variational wave function as compact as possible (in a sense of number of variational parameters and/or basis sets). At first, the explicitly correlated basis were introduced [1,2] now called as the Hylleraas basis

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = e^{-\frac{1}{2}s} \sum c_{lmn} s^l u^m t^m, \\ s = r_1 + r_2, \quad u = r_{12}, \quad t = -r_1 + r_2,$$

then it became clear that at least for the ground state of the helium atom it is essential to incorporate into the wave function such peculiarity as the logarithmic behaviour of the type  $R \ln R$  at  $R = (r_1^2 + r_2^2)^{\frac{1}{2}} \rightarrow 0$ , first analytically derived independently by Bartlett and Fock [3]. In 1966, Frankowski and Pekeris (see Table II) introduced the compact representation [4] of the form

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = e^{-\kappa s} \sum c_{lmnij} s^l u^m t^{2m} (s^2 + t^2)^{i/2} (\ln s)^j,$$

and later, in 1984, Freund and co-workers [5] reported even more compact expansion of the same form. Inclusion of the logarithmic term into the variational wave function brought substantial improvement of nonrelativistic energies for the two electron atoms. In 1994, Thakkar and Koga [6] have found a compact expansion without logarithms which uses powers that are not integers nor even half integers. As far as we know none of these compact expansions has been used for analytical evaluation of matrix elements of the Breit interaction.

With advance of computer power basis sets became simplified that allowed for calculation of numerous matrix elements required for relativistic and QED corrections. The efforts were concentrated on a choice of a strategy that defines a sequence of basis functions generated. In [7] the double basis set method with generalized Hylleraas basis functions

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \sum c_{ijk} r_1^i r_2^j r_{12}^k e^{-\alpha r_1 - \beta r_2} \\ + \sum \bar{c}_{ijk} r_1^i r_2^j r_{12}^k e^{-\bar{\alpha} r_1 - \bar{\beta} r_2}$$

were used. This double basis set technique along with full optimization of nonlinear parameters at each basis set yield substantial progress in accuracy. However, the main factor that hinder further advance become the numerical instability due to almost linear dependence of the basis set at large  $N$ .

The work of Goldman [8] is a bit apart of the main path. It recovers the idea of Pekeris [2] to use uncoupled coordinates and orthogonal Laguerre and Jacoby polynomials as basis functions.

The method expounded in our work is a continuation of efforts by Drake and Yan to utilize as much simple basis functions (geminals) as possible.

2. Expansion we want to consider here is very similar to the generalized Hylleraas basis set, but instead of using the polynomials over Hylleraas variables we generate nonlinear parameters in the exponents in a quasi-random manner,

$$r_1^{l_i} r_2^{m_i} r_{12}^{n_i} e^{-\alpha r_1 - \beta r_2 - \gamma r_{12}} \Rightarrow e^{-\alpha_i r_1 - \beta_i r_2 - \gamma_i r_{12}}. \quad (1)$$

This method has been successfully used in calculations [9,10] previously. Obviously, the matrix elements can be evaluated in the same way as for the generalized Hylleraas basis set (1). Moreover, if one replaces real exponents by complex exponents the integrals will remain exactly the same as for the real case. In its strategy the method is very close to the SVM method by Varga, Suzuki [11], where gaussians are exploited instead.

In a formal way, a variational wave function is expanded in a form

$$\psi_0 = \sum_{i=1}^{\infty} \left\{ U_i \operatorname{Re} [\exp(-\alpha_i r_1 - \beta_i r_2 - \gamma_i r_{12})] \right. \\ \left. + W_i \operatorname{Im} [\exp(-\alpha_i r_1 - \beta_i r_2 - \gamma_i r_{12})] \right\} \mathcal{Y}_{l_i l_2}^{LM}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2).$$

Here  $\alpha_i$ ,  $\beta_i$  and  $\gamma_i$  are complex parameters generated in a quasi-random manner [13,14]:

$$\alpha_i = \left\lfloor \frac{1}{2}i(i+1)\sqrt{p_\alpha} \right\rfloor [(A_2 - A_1) + A_1] + \\ + i \left\lfloor \frac{1}{2}i(i+1)\sqrt{q_\alpha} \right\rfloor [(A'_2 - A'_1) + A'_1],$$

$[x]$  designates the fractional part of  $x$ ,  $p_\alpha$  and  $q_\alpha$  are some prime numbers,  $[A_1, A_2]$  and  $[A'_1, A'_2]$  are real variational intervals which need to be optimized. Parameters  $\beta_i$  and  $\gamma_i$  are obtained in a similar way.

An important feature of the method is that it demonstrates a very fast convergence. The general rule which can be inferred experimentally from the use of the method is that increasing of the basis by about 200 functions yields about one additional digit in the variational energy. The minor deficiency is that the basis quickly degenerates when  $N$  increases. Already for moderate  $N \sim 250 - 400$  a quadruple precision is required.

Multiprecision package of Fortran routines MPFUN has been designed by David H. Bailey [12] for computations with floating point numbers of an arbitrary length. Usually it is necessary to make significant changes into Fortran source code in case if Fortran-77 language is used. Fortunately, the author of MPFUN package has developed a translator program that facilitate converting the programs to multiprecision drastically. In general, two directives incorporated as comments in a source code are required per one routine. For example a source code for the considered variational method has been transformed to multiprecision version within two hours of manual work. Eventually a code we've gotten has been tested on a personal computer with the Celeron 500 MHz processor. For one run with the basis of  $N = 1400$  functions and 40 decimal digits it requires about 3 hours.

For users of Fortran-90 no preprocessor is needed due to new advanced features of Fortran-90, such as derived data types and operator extensions.

$N$	$E$ (a.u.)
1400	-2.90372437703411959629
1600	-2.903724377034119597843
1800	-2.9037243770341195981964
2000	-2.9037243770341195982713
2200	-2.9037243770341195982955
extrapolation	-2.903724377034119598306(10)

TABLE I. Variational energy (in a.u.) of the helium ground state as a function of  $N$ , the number of basis functions.

In our calculations for the helium ground state four basis sets with independently optimized nonlinear parameters were used. These sets were built up like a pine tree. The first layer was tuned to approximate the general behaviour of the solution at intermediate and large  $r_1$  and  $r_2$ . The second layer was chosen to be flexible in a smaller region of  $r_1$  and  $r_2$  and so forth. A detailed optimization was performed for the sets with total  $N = 1400$

and  $N = 1600$ . Quadruple precision was not sufficient at these  $N$  and we used the multiprecision version of the program with 40 significant decimal digits. Further calculations with  $N = 1800 - 2200$  were performed with 48 significant digits and only partial optimization of the parameters of the last layer (corresponding to the region where the logarithmic behaviour is the most essential) was done. Some optimization of a distribution of  $n_i$  between the layers ( $N = n_1 + n_2 + n_3 + n_4$ ) was carried out as well.

As can be seen from the Table II the present result extends the accuracy of the nonrelativistic ground state energy for the helium atom by as much as 3 decimal digits.

	$N$	$E$ (a.u.)
Frankowski and Pekeris [4]	246	-2.9037243770326
Freund, Huxtable, and Morgan III [5]	230	-2.9037243770340
Thakkar and Koga [6]	308	-2.9037243770341144
Drake and Yan [7]	1262	-2.90372437703411948
Goldman [8]	8066	-2.903724377034119594
This work	2200	-2.903724377034119598296

TABLE II. Comparison of the ground state energy of the helium atom obtained in this work with other theoretical calculations.

Second case is the hydrogen molecular ion ground state that represent an other limit of mass distribution of constituents with one light and two heavy particles. For this case it is especially essential that we introduce complex exponents, because it is the most natural way to suit the oscillatory behaviour of the vibrational motion in the wave function. In this case (see Table III) again 40 decimal digits have been used for  $N = 1400 - 1800$  and 48 decimal digits for large  $N$  to provide the numerical stability of the calculations. Table IV demonstrates progress in obtaining variational nonrelativistic energy for this state. The accuracy is extended by as much as 4 additional digits.

$N$	$E$ (a.u.)
1400	-0.597139063123404975
1600	-0.597139063123405047
1800	-0.5971390631234050655
2000	-0.5971390631234050710
2200	-0.5971390631234050740
extrapolation	-0.597139063123405076(2)

TABLE III. Variational energy (in a.u.) of the positive hydrogen ion ground state as a function of  $N$ , the number of basis functions.

	$N$	$E$ (a.u.)
Grémaud, Delande and Billy [15]	31746	-0.597139063123
Rebane and Filinsky [16]		-0.59713906312340
Moss [17]		-0.5971390631234
This work	2200	-0.597139063123405074

TABLE IV. Comparison of the ground state energy of the positive hydrogen molecular ion obtained in this work with other theoretical calculations.  $m_p = 1836.152701m_e$ .

In Table V the other examples are summarized. A negative positronium ion demonstrates a limit of three particles of equal masses. The second and third cases are applications of the method to the states with nonzero angular momentum. The last example in this Table is of special proud. That is the last vibrational state in a series of  $S$ -states of the hydrogen molecular cation, and that is the first variational confirmation of the existence of this state (the binding energy corresponding to the cited value is  $0.74421(2) \text{ cm}^{-1}$ ). The accuracy of the artificial channels scattering method [21] is presumably better, however, wave functions are not forthcoming with this method that makes difficult calculation of physical properties of the state other than energy.

system		$E$
$e^-e^-e^+$	This work	-0.2620050702329801077(3)
	[18]	-0.262005070232976
$\text{He}(2^3P)$	This work	-2.13316419077928310(2)
	[19]	-2.13316419077927(1)
$^4\text{He}^+\bar{p}(L=35, v=0)$	This work	-2.98402095449725(1)
	[20]	-2.98402094
$\text{H}_2^+(L=0, v=19)$	This work	-0.4997312306
	[21]	-0.49973123063

TABLE V. Other examples of three-body calculations. ( $L$  is the total angular momentum,  $v$  is the vibrational quantum number.)

3. One may say that this high accuracy is redundant and has no physical meaning. But obviously, it shows the power of modern computers and theirs ability to solve the quantum three-body problem to any required accuracy. On the other hand, uncertainty in the variational wave function approximately as much as the square root of the uncertainty in the variational energy and is about  $10^{-9} - 10^{-10}$ . This accuracy does not look redundant. These results prove that the nonrelativistic bound state three-body problem is now satisfactorily solved and the main efforts should be addressed to relativistic and QED effects.

The other advantage of the method is the simplicity of the basis functions that allows for evaluate analytically

relativistic matrix elements of the Breit Hamiltonian. It is possible as well to evaluate analytically the vacuum polarization term (Uehling potential) [22] and to build up an effective numerical scheme for the one-loop self-energy corrections [23]. These features make the considered variational method to be highly powerful universal tool for studying the three-body problem.

This work has been partially supported by INTAS Grant No. 97-11032, which is gratefully acknowledged.

- 
- [1] E.A. Hylleraas, Z. Physik **54**, 347 (1929); S. Chandrasekhar and G. Herzberg, Phys. Rev. **98**, 1050 (1955); T. Kinoshita, Phys. Rev. **105**, 1490 (1956).
  - [2] C.L. Pekeris, Phys. Rev. **112**, 1649 (1958); **115**, 1216 (1959).
  - [3] J.H. Bartlett, Phys. Rev. **51**, 661 (1937); V.A. Fock, Izvest. Akad. Nauk S.S.S.R. Ser. Fiz. **18**, 161 (1954).
  - [4] K. Frankowski and C.L. Pekeris, Phys. Rev. **146**, 46 (1966); **150**, 366(E) (1966).
  - [5] D.E. Freund, B.D. Huxtable, and J.D. Morgan III, Phys. Rev. A **4**, 516 (1971).
  - [6] A.J. Thakkar and T. Koga, Phys. Rev. A **50**, 854 (1994).
  - [7] G.W.F. Drake and Zong-Chao Yan, Chem. Phys. Lett. **229**, 486 (1994).
  - [8] S.P. Goldman, Phys. Rev. A **57**, R677 (1998).
  - [9] S.A. Alexander, H.J. Monkhorst, Phys. Rev. A **38**, 26 (1988).
  - [10] A.M. Frolov and V.D. Efros Pis. Zh. Eksp. Teor. Fiz. **39**, 544 (1984) [Sov. Phys.-JETP Lett. **39**, 449 (1984)]; A.M. Frolov, and V.H. Smith, Jr., J. Phys. B **28**, L449 (1995).
  - [11] K. Varga and Y. Suzuki, Phys. Rev. C **52**, 2885 (1995); Phys. Rev. A **53**, 1907 (1996).
  - [12] D.H. Bailey, ACM Trans. Math. Softw. **19**, 288 (1993); **21**, 379 (1995); see also web-site: [www.netlib.org](http://www.netlib.org).
  - [13] A.M. Frolov, and V.H. Smith, Jr., J. Phys. B **28**, L449 (1995).
  - [14] V.I. Korobov, D. Bakalov, and H.J. Monkhorst, Phys. Rev A **59**, R919 (1999).
  - [15] B. Grémaud, D. Delande, and N. Billy, J. Phys. B: At. Mol. Opt. Phys. **31**, 383 (1998).
  - [16] T.K. Rebane and A.V. Filinsky, Phys. At. Nuclei **60**, 1816 (1997).
  - [17] R.E. Moss, J. Phys. B: At. Mol. Opt. Phys. **32**, L89 (1999).
  - [18] A.M. Frolov, Phys. Rev. A **60**, 2834 (1999).
  - [19] G.W.F. Drake and Zong-Chao Yan, Phys. Rev. A **46**, 2378 (1992).
  - [20] Y. Kino, M. Kamimura and H. Kudo, Nucl. Phys. A, **631**, 649 (1998).
  - [21] R.E. Moss, Mol. Phys. **80**, 1541 (1993).
  - [22] P. Petelenz and V.H. Smith, Jr., Phys. Rev. A **35**, 4055 (1987); **36**, E4529 (1987).
  - [23] V.I. Korobov and S.V. Korobov, Phys. Rev A **59**, 3394 (1999).